

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

P/61802-PCT

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10 / 048105

INTERNATIONAL APPLICATION NO.
PCT/GB00/02893INTERNATIONAL FILING DATE
July 27, 2000PRIORITY DATE CLAIMED
July 28, 1999TITLE OF INVENTION **HYDROCARBON FUEL PROCESSOR CATALYST**APPLICANT(S) FOR DO/EO/US **Martin Roy HARRISON; Giles HUMPHSTON; Paul Christopher OSBOND**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371 (f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☒ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: **Receipt Acknowledgment Postcard**

U.S. APPLICATION NO. 10/048105		INTERNATIONAL APPLICATION NO. PCT/GB00/02893		ATTORNEY'S DOCKET NUMBER P/61802-PCT	
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21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,040.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY 	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	21 - 20 =	1	x \$18.00	\$18.00	
Independent claims	3 - 3 =	0	x \$84.00	\$0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$280.00	
TOTAL OF ABOVE CALCULATIONS =				\$908.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$908.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$0.00	
TOTAL NATIONAL FEE =				\$908.00	
Fee for recording the enclosed assignment (37 CFR 1.21 (h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$0.00	
TOTAL FEES ENCLOSED =				\$908.00	
				Amount to be refunded:	\$
				charged:	\$

a. ☒ A check in the amount of **\$908.00** to cover the above fees is enclosed.

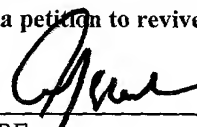
b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-1145. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

KIRSCHSTEIN, OTTINGER, ISRAEL & SCHIFFMILLER, P.C.
 489 Fifth Avenue
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SIGNATURE: 

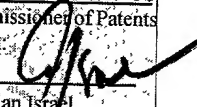
Alan Israel
 NAME
27,564
 REGISTRATION NUMBER

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Docket No. P/61802

PATENTS
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

I hereby certify that this correspondence is being deposited with the U.S. Postal Service as Express Mail No. EL337 911 913 US in an envelope addressed to: Box: PCT, Commissioner of Patents and Trademarks, Washington, D.C. 20231, on January 25, 2002 (date) 
Alan Israel
Reg. No. 27,564

International Application No.: PCT/GB00/02893
International Filing Date : July 27, 2000
In re: Application of : Martin Roy HARRISON, et al.
Deposited : January 25, 2002
For : HYDROCARBON FUEL PROCESSOR CATALYST

New York, New York
January 25, 2002

PRELIMINARY AMENDMENT

BOX: PCT
Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

Prior to calculation of the filing fee and before examination, kindly amend the above captioned application as follows:

IN THE CLAIMS:

Please cancel claims 1-20, without prejudice.

Please add the new set of claims 21-41 as set forth on the enclosed pages.

IN THE ABSTRACT:

Delete the "Abstract" on the PCT cover sheet and replace it with the "Abstract of the Disclosure" set forth on a separate sheet attached hereto.

REMARKS

An abstract has been provided on a separate sheet; and the claims have been amended to conform to U.S. practice.

Wherefore, an early action on the merits is earnestly solicited.

Respectfully submitted,

KIRSCHSTEIN, OTTINGER, ISRAEL & SCHIFFMILLER, P.C.

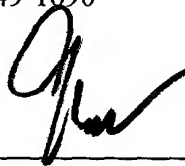
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10/048105

531 Rec'd PCT/PT 25 JAN 2002

ABSTRACT OF THE DISCLOSURE

A catalyst for use in a hydrocarbon fuel processor for converting, or reforming, a hydrocarbon fuel such as diesel into a simple fuel, most especially hydrogen, comprises a rare earth metal (M) cobalt oxide ($MCoO_3$) having a perovskite structure. In one composition, the catalyst comprises a solid solution having the perovskite structure of the rare earth metal cobalt oxide, preferably lanthanum cobalt oxide ($LaCoO_3$), and an alkaline earth metal cobalt oxide, preferably strontium cobalt oxide ($SrCoO_3$). To further enhance the catalytic activity, the catalyst can additionally include a noble metal oxide such as platinum or ruthenium.

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PROPOSED NEW CLAIMS

21. A use of a rare earth metal cobalt oxide having a perovskite crystal structure as a catalyst in a hydrocarbon fuel processor for processing a hydrocarbon fuel into a simple fuel.

22. The use according to claim 21, in which the catalyst further includes one of a noble metal and a noble metal oxide.

23. The use according to claim 21, in which the catalyst comprises a solid solution having the perovskite crystal structure of the rare earth metal cobalt oxide and an alkaline earth metal cobalt oxide.

24. The use according to claim 21, in which the rare earth metal is lanthanum.

25. The use according to claim 22, in which the one of the noble metal and noble metal oxide is one of ruthenium and ruthenium oxide.

26. The use according to claim 22, in which the one of the noble metal and noble metal oxide is one of platinum and platinum oxide.

27. The use according to claim 23, in which the alkaline earth is selected from a group consisting of calcium, strontium and barium.

28. The use according to claim 23, in which alkaline earth metal cobalt oxide is in a proportion up to 50% of the catalyst.

29. The use according to claim 22, in which the one of the noble metal and noble metal oxide is included up to 2 mole% of the catalyst.

30. The use according to claim 21, in which the catalyst undergoes thermal decomposition such that its surface becomes coated with catalytically active lanthium oxide, hydrated lanthium oxide and cobalt metal particles.

31. The use according to claim 21, wherein the simple fuel is hydrogen.
32. A hydrocarbon fuel processor catalyst, comprising: a rare earth metal cobalt oxide having a perovskite crystal structure.
33. The catalyst according to claim 32, and further including one of a noble metal and a noble metal oxide.
34. The catalyst according to claim 32, and including a solid solution having the perovskite crystal structure of the rare earth metal cobalt oxide and an alkaline earth metal cobalt oxide.
35. The catalyst according to claim 32, in which the rare earth metal is lanthanum.
36. The catalyst according to claim 33, in which the one of the noble metal and noble metal oxide is one of ruthenium and ruthenium oxide.
37. The catalyst according to claim 33, in which the one of the noble metal and noble metal oxide is one of platinum and platinum oxide.
38. The catalyst according to claim 34, in which the alkaline earth is selected from a group consisting of calcium, strontium and barium.
39. The catalyst according to claim 34, in which the alkaline earth metal cobalt oxide is in a proportion up to 50% of the catalyst.
40. The catalyst according to claim 33, in which the one of the noble metal and noble metal oxide is included up to 2 mole % of the catalyst.
41. A hydrocarbon fuel processor for converting a hydrocarbon fuel to hydrogen, comprising: a catalyst comprising a rare earth metal cobalt oxide having a perovskite crystal structure.

HYDROCARBON FUEL PROCESSOR CATALYST

This invention relates to a hydrocarbon fuel processor catalyst for converting or reforming a hydrocarbon fuel into a simple fuel and is more especially, although not exclusively, concerned with a catalyst for converting a liquid hydrocarbon fuel to hydrogen for use in a fuel cell.

Fuel cells offer the promise of smaller and lighter weight power sources that are potentially instantaneous and silent in their operation. For example, fuel-cell powered vehicles are currently being developed as a more fuel-efficient and less polluting alternative to the internal combustion engine.

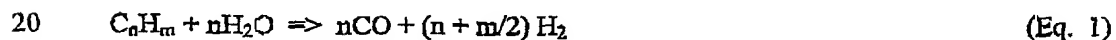
For large scale, generally static applications, solid oxide fuel cells can be used. Due to their high operating temperature, typically around 800°C, such fuel cells are able to directly utilise fuels such as methanol, methane or natural gas. Whilst suitable for large scale operation, such as combined heat and power facilities for building complexes, these cells are not suited to mobile applications as they are bulky and have a slow start up due to their high operating temperature.

For mobile applications such as vehicles, polymer fuel cells have been proposed. Due to their relatively low operating temperature (typically around 80°C), such cells offer a rapid start up as required in these applications. Polymer fuel cells operate most efficiently on pure hydrogen, but it is currently difficult to store hydrogen on board the vehicle in a safe and cost effective way. A fuel processor or reformer converts

hydrocarbon fuels to hydrogen gas, potentially enabling fuel-cell powered vehicles to run on fuels which are widely available today, such as liquefied petroleum gas (LPG), paraffin, gasoline or diesel.

5 Compact fuel processors suitable for use on vehicles have already been developed for lighter hydrocarbon fuels such as methanol. However, these processors are usually specific to one type of fuel and require a high purity feed since impurities such as sulphur are very detrimental to the reforming catalyst and can permanently deactivate it. It is therefore desirable to produce a compact fuel processor that can extract
10 acceptable amounts of hydrogen from a wide range of commercial fuels and function without adjustment as the fuel type changes. These new reforming catalysts should be much more resistant to coking or sulphur deactivation than the currently available catalysts.

15 A number of different designs of fuel processor have been proposed for converting hydrocarbon fuels to hydrogen which are based on a steam-reforming reaction in which vaporised hydrocarbon fuel is reacted with steam (H_2O). This reaction can be represented by the following endothermic equation:



A catalyst may optionally be used to increase the reaction rate, though high temperatures and pressures are still required. As can be seen from the equation, the carbon in the hydrocarbon fuel is converted to carbon monoxide by oxidation using

the oxygen provided by the steam whilst the hydrogen in the fuel and steam is released as hydrogen gas. The optimum steam to carbon ratio ($H_2O:C$) depends on the processor conditions (temperature and pressure), but invariably this ratio increases as the carbon content of the hydrocarbon increases. Large quantities of steam are therefore required for heavy fuels such as diesel and this demands a high energy input to vaporise the water, leading to a poor thermal efficiency, a slow response time and a slow start up from cold.

An alternative, potentially more responsive, process relies upon the partial oxidation of the hydrocarbon fuel. This can be represented by the following exothermic reaction:



The optimum oxygen to carbon ratio ($O_2:C$) depends on the processor conditions and increases as the carbon content of the hydrocarbon increases. Again a catalyst can be used to increase the reaction rate. To prevent clogging of the catalyst, most typically by coke deposition, the initial combustion can occur at high temperatures in the absence of a catalyst to break the hydrocarbon fuel down to simpler molecules. The gas stream is then passed over a catalyst to further break down the molecules into carbon monoxide and hydrogen. Although such a processor exhibits a faster response it has relatively lower hydrogen conversion efficiency than a steam reforming system.

It has been further proposed to provide fuel processors which use an "autothermal reforming process" to convert the hydrocarbon fuel to hydrogen and carbon monoxide with a combination of the above two processes. In such a processor the heat liberated by the exothermic partial oxidation reaction (Eq. 2) is used to drive the endothermic steam reforming reaction (Eq. 1) thereby improving the overall thermal efficiency of the processor. Different specialist catalysts may be used in physically separate partial oxidation and steam reforming reaction volumes within the processor or alternatively the partial oxidation and steam reforming reactions can take place over a common catalyst bed. The latter produces a simpler system design but places great demands on the catalyst material. In one known design the vaporised fuel is mixed with air and steam and then injected into an enclosure containing the granulated catalyst material.

At present the known fuel processors capable of processing heavier hydrocarbons fuels such as diesel are not ideally suited to small scale mobile applications. Firstly, the endothermic nature of the steam generating and steam reforming processes does not readily lend itself to operating efficiently on a small scale. Secondly, the comparatively high carbon content (high carbon to hydrogen ratio C:H) of many hydrocarbon fuels such as diesel clogs the catalyst through the deposition of coke (carbon) on the surface of the catalyst which blocks access to the active surface of the catalyst. Thirdly, the high sulphur level in many heavier hydrocarbon fuels poisons, that is reduces the activity of, the known catalysts used in the steam-reforming process thereby degrading the conversion efficiency.

The known catalysts for fuel conversion, or reforming, comprise base metals (such as nickel), noble metals (such as platinum), or a mixture of these, either in powdered form or as a coating on the surface of an inert ceramic substrate. The noble metal is generally dispersed in the form of small particles in order to minimise the metal cost and maximise the surface activity. These catalysts are, however, adversely affected by sulphur present in the fuels and are vulnerable to coking since there is no mechanism to remove the carbon from the catalyst surface once it has been deposited. There is therefore considerable scope for the development of improved catalyst systems that are cheaper, more efficient and more versatile than the current materials.

The present invention has arisen in an endeavour to develop a new catalyst formulation which is suitable for use with diesel and other heavy hydrocarbon fuels in an autothermal fuel processing system, and which is in part at least resistant to both sulphur poisoning and clogging with coke deposition.

According to the present invention there is provided use of a rare earth metal cobalt oxide ($MCoO_3$) having the perovskite crystal structure as a catalyst in a hydrocarbon fuel processor for converting or reforming a hydrocarbon fuel into a simple fuel most especially hydrogen. Due to its high oxygen ion mobility at temperatures at which such fuel processors operate, typically less than 800°C , use of such a catalyst offers a number of advantages over the known catalysts: (i) the presence of the oxygen ions at the catalyst surface coating promotes the fuel breakdown process; (ii) the oxygen ions oxidise any carbon or contaminants which may be deposited on the catalyst surface coating during the fuel breakdown reaction and this reduces the likelihood of the catalyst becoming clogged, especially when using a high C:H fuel such as diesel, and

(iii) the oxygen ions prevent contaminants which might otherwise de-activate the catalyst, such as sulphur, becoming bonded to the surface coating. The inventors further believe that during the use of the catalyst the surface decomposes and becomes covered with a catalytically active coating of rare earth oxide, hydrated rare-earth oxide and cobalt metal particles which prevents the catalyst's activity becoming rapidly degraded by carbon deposition and/or by the effects of sulphur or other contaminants. A catalyst in accordance with the invention can therefore be said to be self cleaning. In contrast the known catalysts comprise an inert support structure with a catalytically active coating which is vulnerable to the effects of carbon and/or sulphur.

Advantageously the catalyst further includes a noble metal or noble metal oxide. Such a catalyst offers a high catalytic activity in which the oxygen ions provide a scouring activity which protects the activity of the noble metal or noble metal oxide at the operating temperature of the fuel processor. In one embodiment the noble metal or noble metal oxide comprises platinum or platinum oxide. In a particularly preferred embodiment the noble metal or noble metal oxide comprises ruthenium or ruthenium oxide which is found to give at least the same activity but which has a cost appreciably less than that of platinum. Preferably the noble metal or noble metal oxide is present up to 2 mole %.

Preferably the catalyst further comprises a solid solution having the perovskite crystal structure of the rare earth metal cobalt oxide and an alkaline earth metal cobalt oxide, such as for example a solid solution of lanthanum cobalt oxide and strontium cobalt

oxide. The substitution of the rare earth ions by alkaline earth ions increases the number of vacant sites for oxygen within the perovskite crystal structure thereby increasing the number and the mobility of oxygen ions within the crystal lattice. Advantageously the alkaline earth metal cobalt oxide is included in a proportion of up to 50%.

In a preferred catalyst composition the alkaline earth metal comprises strontium although calcium or barium can be used.

According to a second aspect of the invention a hydrocarbon fuel processor catalyst is characterised by comprising a rare earth metal cobalt oxide having the perovskite structure as described above. According to a third aspect of the invention a hydrocarbon fuel processor for converting a hydrocarbon fuel to hydrocarbon incorporates a catalyst as described above.

Nine catalyst compositions in accordance with the invention will now be described by way of example only. The first catalyst composition described is lanthanum cobalt oxide (LaCoO_3) having the perovskite crystal structure. Lanthanum oxide (La_2O_3) powder was heated in air at 1000°C to decompose any Lanthanum Hydroxide $\text{La}(\text{OH})_3$ present in the material to give single phase La_2O_3 . The single phase La_2O_3 material was mixed with cobalt oxide (CoO) powder in appropriate weights to give the LaCoO_3 and the mixture ball-milled for 4 hours in approximately 40 gramme batches and then calcined (heated in a furnace) in air at 1050°C for 3 hours. The ceramic product after calcining was crushed and graded into a desired particle size,

approximately 1-10 μ m, prior to testing. As will be appreciated by those skilled in the art, the desired particle size will depend on the type of fuel processor and can accordingly be readily optimised for a required application.

5 X-ray diffraction studies of the material showed the crystal structure to be a substantially phase pure perovskite crystal structure. The perovskite crystal structure is that which exists in mineral perovskite CaTiO_3 and which is commonly adopted in compounds having the general formula ABO_3 where A is a relatively large cation (lanthanum in this example) and B is a relatively smaller cation (cobalt in this
10 example). The B cations are each surrounded by a maximum of six oxygen ions to form a three-dimensional network of corner shared octohedra whilst the A cations occupy the interstices between the octohedra. The facile mixing of cations with different valences on both the A and B sites combined with the variable valence nature of the B cations promotes a complex defect structure which can provide a high
15 mobility for the oxygen ions. X-ray diffraction patterns of samples showed that a significant quantity of La_2O_3 still remained in the samples which could not be eliminated by calcining for longer periods. This is believed to be a consequence of the CoO actually being a mixture of CoO and Co_3O_4 , the latter of which cannot be readily converted to single CoO by heat treatment. To compensate for this a 5 mole
20 % excess of CoO was added to the starting mixture. Samples prepared in this way showed only a trace of La_2O_3 remaining in the final composition.

Eight other catalyst compositions were synthesised which are shown in Table 1 below. First, samples were prepared containing the noble metals ruthenium (Ru) and

platinum (Pt) by calcining mixtures of La_2O_3 , and PtO_2 or RuO_2 with a 5 mole % excess of CoO (compositions 2 and 3 in the table). Scanning electron microscopy analysis of the platinum oxide and ruthenium oxide powders showed that it was an extremely fine powder with a primary particle size probably well below $0.1\mu\text{m}$ (dimensions beyond the resolution of the scanning electron microscope equipment available at the time of analysis). The energy-dispersive X-ray analysis in a scanning electron microscope of single grains of the resultant catalyst material confirmed that the platinum/ruthenium was present either within the grains or as a coating on the surface of the grains. No particles could be identified which were very rich in platinum/ruthenium, suggesting that the noble metal is not present as a second phase (either as the metal or as the oxide).

Catalysts containing the noble metal and/or noble metal oxide were found to exhibit an enhanced activity compared to LaCoO_3 . This is attributed to the catalytic activity of the noble metal which is protected against clogging and or contamination by the scouring effect of the high mobility oxygen ions from the LaCoO_3 perovskite crystal structure. This being said it will be appreciated that the concentration of noble metal is selected such that there is sufficient LaCoO_3 to provide adequate cleaning of the metal. Test results indicate that ruthenium is at least as effective as platinum but has the substantial advantage of being much lower in cost.

Composition 1 LaCoO_3	Composition 4 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$	Composition 7 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$
Composition 2 LaCoO_3 + 2 mole % PtO_2	Composition 5 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ + 2 mole % PtO_2	Composition 8 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ + 2 mole % PtO_2
Composition 3 LaCoO_3 + 2 mole % RuO_2	Composition 6 $\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3$ + 2 mole % RuO_2	Composition 9 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ + 2 mole % RuO_2

Table 1: Catalyst compositions.

In the remaining compositions (4 to 9), a fraction of the lanthanum ions was replaced by strontium (Sr) ions to form a solid solution of LaCoO_3 and SrCoO_3 . A 5 mole % excess of CoO was also added to the starting mixtures of these compositions. The calcination temperature needed for the complete elimination of La_2O_3 decreased as the strontium content increased, and was found to be 950°C for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$. The complete list of synthesized samples is given in Table 1. The substitution of the lanthanum ions by strontium ions increases the number of vacant sites for oxygen within the perovskite structure thereby increasing the number and the mobility of oxygen ions within the crystal lattice.

Testing of the catalysts with diesel and other hydrocarbon fuels in a fuel processor showed the material to have good catalytic activity which was resistant both to clogging by coke or other contaminants and to poisoning from sulphur. The following results pertain to Composition 3 in the above Table 1. This composition
5 was tested with a range of liquid hydrocarbon fuels including liquid petroleum gas (LPG - a mixture of propane and butane), paraffin, gasoline and diesel.

As far as possible, the same test procedure was used for each of these fuels. The steam to carbon ratio ($H_2O:C$) and air to carbon ratio ($O_2:C$) ratios were fixed during
10 initial temperature-programmed tests. The feed temperature was then ramped up from approximately 350°C to 850°C and then back down to 350°C, while the hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and heavier hydrocarbon content of the dried output gas stream were measured. The aim was to determine whether coke deposition or deactivation with sulphur occurred over a
15 portion of the temperature ramp. For example, coke deposition often occurred at low temperatures but was normally burnt off by the catalyst at higher temperatures. The plot of the hydrogen content versus temperature then showed a hysteretic effect where, at a selected feed temperature, the hydrogen content was lower when the catalyst temperature was raised than when the catalyst temperature was lowered.

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Following the temperature ramp, the temperature of the fuel, air and steam feed was held constant at selected values, typically 600°C or 800°C. The composition of the feed, that is steam to carbon ratio ($H_2O:C$) and air to carbon ratio ($O_2:C$), more especially the ratio of the oxygen content of the air to carbon, were then altered and

the measurements repeated to determine the conditions providing the best catalytic activity. The steam and air to carbon ratios used are shown in Table 2. These conditions were chosen because they resulted in the near autothermal conversion of the heavier liquid fuels (paraffin, gasoline and diesel).

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H ₂ O:C	O ₂ :C
1.0	0.38
1.5	0.50
2.0	0.64

Table 2: Steam (H₂O:C) and air (O₂:C) to carbon ratios used for the catalyst tests.

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The results obtained are summarised in Table 3. These data were obtained while the feed temperature was held at a constant value, and shows the hydrogen (H₂), carbon monoxide (CO) and methane (CH₄) content of the output gas stream under the conditions that generated the highest hydrogen content for each tested fuel. As is discussed below the remainder of the output gas stream comprises nitrogen and carbon dioxide the former resulting from the use of air rather than oxygen in the reaction process. In general, this occurred under near autothermal conditions using a H₂O:C ratio of 1.0 and a O₂:C ratio of 0.38. However, the use of LPG under these conditions gave very high reactor temperatures in excess of ~1000°C. The use of a higher H₂O:C ratio and a lower O₂:C ratio is therefore beneficial with this fuel since

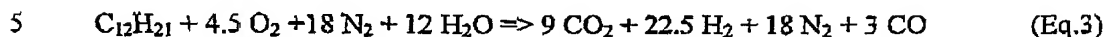
this maintained the catalyst bed at a lower temperature and also increased the concentration of hydrogen in the output gas stream

Fuel	Test Results				Test Conditions		
	% content of output gas stream			Catalyst temp. (°C)	O ₂ :C	H ₂ O:C	Feed temp. (°C)
	H ₂ max.	CO	CH ₄				
LPG	32.9	11.8	1.2	1007	0.38	2.0	600
	28.1	12.9	2.0	980	0.38	2.0	800
Paraffin	40.5	10.1	0.5	587	0.38	1.0	600
	35.2	15.2	2.6	758	0.38	1.0	800
Unleaded gasoline	13.5	7.6	0.9	743	0.50	1.0	600
	21.6	13.2	3.7	781	0.38	1.0	800
City diesel	34.9	9.5	0.6	594	0.38	1.0	600
	32.5	13.9	2.4	755	0.38	1.0	800

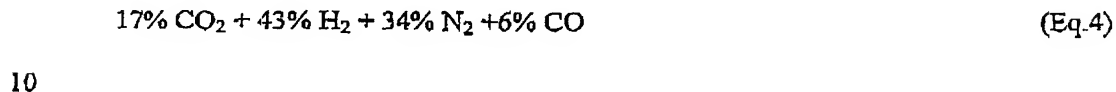
5 Table 3: Test results and test conditions for various hydrocarbon fuels using the catalyst composition 3.

10 The small concentrations of fuel or other hydrocarbons exiting the reactor (less than 5%) indicate that near complete conversion was obtained for LPG, paraffin and diesel. For all of these fuels, the maximum hydrogen content under these conditions is calculated to fall within the range 42%-48%. Taking diesel as an example, the

average molecular weight of this fuel is assumed to be ~170 and the chemical composition approximates to $C_{12}H_{21}$. For $H_2O:C = 1$ and $O_2:C = 0.38$, the reaction stoichiometry for complete conversion would then be:



The composition of the reformat would therefore be:



so that the maximum hydrogen content extractable from this fuel under these conditions is ~43%.

15 The conversion efficiency for gasoline was lower than that of the other tested fuels, and this is attributed to the higher sulphur content of this fuel. The LPG, paraffin and city diesel had a very low sulphur contents (less than 10ppm) while the unleaded gasoline had a much higher sulphur content of 100ppm. However, the temperature programmed data obtained with gasoline indicate that retained sulphur species on the catalyst surface desorbed at high temperatures around 800°C so that operation under
20 these conditions at least partially restored the catalytic activity.

The inventors believe that the good catalytic properties of these materials are due to their high oxygen ion mobility at temperatures for use in such fuel processors, typically less than 800°C. Firstly the presence of the oxygen ions at the catalyst

surface promotes the fuel breakdown process. Secondly the oxygen ions oxidise any carbon or contaminants which may be deposited on the catalyst surface during the fuel breakdown reactions thereby reducing the likelihood of catalyst clogging, especially when using a fuel having high carbon to hydrogen ratio such as diesel.

5 Thirdly the oxygen ions prevent contaminants, such as sulphur, becoming bonded to the surface which might otherwise de-activate the catalyst. It is believed that during the use of the catalyst a certain degree of decomposition of the Perovskite crystal structure occurs at the material surface such that the surface of the material becomes covered with a catalytically active coating of lanthium oxide (La_2O_3) and cobalt metal
10 particles which prevents the catalyst's activity becoming rapidly degraded by carbon deposition and/or by the effect of sulphur or other contaminants.

It will be appreciated that the present invention is not limited to the specific compositions described and that further compositions are envisaged which are within
15 the scope of the invention. For example the basic catalyst has been described in relation to LaCoO_3 though other rare earth metal (M) cobalt oxides (MCoO_3) having the perovskite crystal structure could be used. Furthermore it is envisaged to add other noble metals or noble metal oxides or a mixture thereof. Further it will be appreciated that solid solutions with alkaline earth metals other than strontium such
20 as calcium or barium can be used to increase the oxygen ion mobility. Furthermore it will be appreciated that a catalyst in accordance with the invention can be used for other types of hydrocarbon fuels other than diesel and is especially suited to use with heavier hydrocarbon fuels.

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CLAIMS

1. Use of a rare earth metal cobalt oxide having the perovskite crystal structure as a catalyst in a hydrocarbon fuel processor for converting or reforming a hydrocarbon fuel into a simple fuel most especially hydrogen.
2. Use according to Claim 1 in which the catalyst further includes a noble metal or noble metal oxide.
3. Use according to Claim 1 or Claim 2 in which the catalyst comprises a solid solution having the perovskite crystal structure of the rare earth metal cobalt oxide and an alkaline earth metal cobalt oxide.
4. Use according to any preceding claim in which the rare earth metal is lanthanum.
5. Use according to any one of Claims 2 to 4 in which the noble metal or noble metal oxide is ruthenium or ruthenium oxide.
6. Use according to any one of Claims 2 to 4 in which the noble metal or noble metal oxide is platinum or platinum oxide.
7. Use according to Claim 3 or to any one of Claims 4 to 6 when dependent on Claim 3 wherein the alkaline earth is calcium, strontium or barium.

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8. Use according to Claim 3 or any one of Claims 4 to 7 when dependent on Claim 3 in which the catalyst further includes the alkaline earth metal cobalt oxide in a proportion up to 50%.
9. Use according to Claim 2 or any one of Claims 3 to 8 when dependent on Claim 2 in which the noble metal or noble metal oxide is included up to 2 mole %.
10. Use according to any preceding claim in which the catalyst undergoes thermal decomposition such that its surface becomes coated with catalytically active lanthium oxide, hydrated lanthium oxide and cobalt metal particles.
11. A hydrocarbon fuel processor catalyst characterised by comprising a rare earth metal cobalt oxide having the perovskite crystal structure.
12. A catalyst according to Claim 11 and further including a noble metal or noble metal oxide.
13. A catalyst according to Claim 11 or Claim 12, which comprises a solid solution having the perovskite crystal structure of the rare earth metal cobalt oxide and an alkaline earth metal cobalt oxide.
14. A catalyst according to any one of Claims 11 to 13 in which the rare earth metal is lanthanum.

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15. A catalyst according to any one of Claims 12 to 14 in which the noble metal or noble metal oxide is ruthenium or ruthenium oxide.
16. A catalyst according to any one of Claims 12 to 14 in which the noble metal or noble metal oxide is platinum or platinum oxide.
17. A catalyst according to Claim 13 or to any one of Claims 14 to 16 when dependent on Claim 13 in which the alkaline earth is calcium, strontium or barium.
18. A catalyst according to Claim 13 or any one of Claims 14 to 17 when dependent on Claim 13 and including the alkaline earth metal cobalt oxide in a proportion up to 50%.
19. A catalyst according to Claim 12 or any one of Claims 13 to 18 when dependent on Claim 12 and comprising including, the noble metal or noble metal oxide up to 2 mole %.
20. A hydrocarbon fuel processor for converting a hydrocarbon fuel to hydrogen incorporating a catalyst according to any one on Claims 11 to 19.

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(54) Title: HYDROCARBON FUEL PROCESSOR CATALYST

(57) Abstract: A catalyst for use in a hydrocarbon fuel processor for converting, or reforming, a hydrocarbon fuel such as diesel into a simple fuel, most especially hydrogen, comprises a rare earth metal (M) cobalt oxide ($MCoO_3$) having the perovskite structure. In one composition the catalyst comprises a solid solution having the perovskite structure of the rare earth metal cobalt oxide, preferably lanthanum cobalt oxide $LaCoO_3$, and an alkaline earth metal cobalt oxide, preferably strontium cobalt oxide $SrCoO_3$. To further enhance the catalytic activity the catalyst can additionally include a noble metal oxide such as platinum or ruthenium.

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First Named Inventor

HARRISON, MARTIN ROY

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

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Submitted
with Initial Filing

☒ Declaration
Submitted after
Initial Filing

COMPLETE IF KNOWN

Application Number

10/048,105

Filing Date

JANUARY 25, 2002

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

HYDROCARBON FUEL PROCESSOR CATALYST

(Title of the Invention)

the specification of which

☐ is attached hereto
OR

☒ was filed on (MM/DD/YYYY)

July 27, 2000

as United States Application Number or PCT International

U.S. Serial No. 10/048,105,
JANUARY 25, 2002

Application Number

PCT/GB00/02893

and was amended on (MM/DD/YYYY)

(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119 (a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365 (a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
				YES	NO
9917583.8	GB	July 28, 1999 07-28-1999	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input checked="" type="checkbox"/>
PCT/GB00/02893	INTERNATIONAL	07-27-2000			

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

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DECLARATION

ADDITIONAL INVENTOR(S) Supplemental Sheet

Name of Additional Joint Inventor, if any:				<input type="checkbox"/> A petition has been filed for this unsigned inventor			
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Post Office Address							
City		State		Zip		Country	
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<input type="checkbox"/> Additional inventors are being named on supplemental sheet(s) attached hereto							

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